REACTION OF POLYFLUOROALKYL FLUOROSULFATES WITH N-NUCLEOPHILES

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Polyfluoroalkyl fluorosulfates (PFS) react with anhydrous NH_3 and alkylamines to give high yields of polyfluorocarboxylic acid amides [1, 2]. Alkyl- and arylhydrazines which are weaker bases than NH_3 and amines [3] do not react with PFS.

We have found that unsymmetrical dimethylhydrazine (DH) and phenylhydrazine react smoothly with PFS in ether at 0°C to give the corresponding polyfluorocarboxylic acid hydrazides:

$$\underset{(I)-(V)}{R_FCF_2OSO_2F} + H_2NNRR' \rightarrow \underset{(Ia,b)-(Va,b)}{R_FCONHNRR'}$$

$$R = R' = Me\ (a),\ R = H,\ R' = Ph\ (^b).$$

$$R_F = CF_3CFH\ (I),\ HCF_2CF_2 (II),\ CF_3CFCl (III),\ ClCF_2CF_2 (IV),\ Cl(CF_2)_7 (V).$$

Complete conversion of PFS and maximum yields of hydrazides (Ia, b)-(Va, b) are observed upon the use of a 4—5-fold molar excess of the hydrazine, which is explained by the need to bind the acid products formed [1].

An unsuccessful attempt was undertaken to obtrain hydrazide (IIIa) according to Voronkov et al. [4] by the transamination of 2-chlorotetrafluoropropionamide by the action of DH, but more than 70% of the starting amide was recovered after heating the reagent mixture for six days.

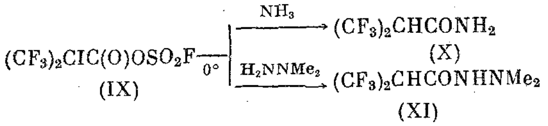
Special interest was found in the reactions of these N-nucleophiles with α-bromo- (VI) and α-iodohexafluoroisobutyl fluorosulfates (VII) which contain rather mobile bromine and iodine atoms. Bubbling of excess NH_3 through a solution of (VI) and (VII) in ether at 0°C gives ester (VIII) and, correspondingly, ethyl bromide or ethyl iodide instead of the expected amides

$$\underset{(VI),\ (VII)}{(CF_3)_2CXCF_2OSO_2F} + NH_3 \rightarrow \underset{(VIII)}{(CF_3)_2CHCOOEt} + EtX$$

$$X = Br,\ I.$$

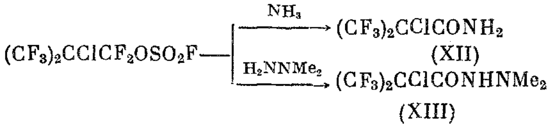
α-Bromohexafluoroisobutyroyl chloride under mild conditions brominates diethyl ether and is thereby converted to ethyl α-hydrohexafluoroisobutyrate (VIII) [5]. The formation of ester (VIII) and ethyl halides in the present reaction is apparently a result of the intermediate formation of the α-bromo- and α-iodohexafluoroisobutyryl fluorides from fluorosulfate (VI) and (VII).

In contrast to (VI) and (VII), α-iodohexafluoroisobutyroyl fluorosulfate (IX) reacts with NH_3 and DH in order to form the amide (X) and N,N-dimethylhydrazide (XI) of α-hydrohexafluoroisobutyric acid, respectively.



$$\underset{(IX)}{(CF_3)_2CIC(O)OSO_2F} \xrightarrow{0°} \begin{cases} \xrightarrow{NH_3} \underset{(X)}{(CF_3)_2CHCONH_2} \\ \xrightarrow{H_2NNMe_2} \underset{(XI)}{(CF_3)_2CHCONHNMe_2} \end{cases}$$

On the other hand, β-chlorooctafluoroisobutyl fluorosulfate reacts with NH_3 and DH under these condiitons to give the amide (XII) and N,N-dimethylhydrazide (XIII) of α-chlorohexafluoroisobutyric acid.



$$(CF_3)_2CClCF_2OSO_2F \begin{cases} \xrightarrow{NH_3} \underset{(XII)}{(CF_3)_2CClCONH_2} \\ \xrightarrow{H_2NNMe_2} \underset{(XIII)}{(CF_3)_2CClCONHNMe_2} \end{cases}$$

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TABLE 1. ^{1}H and ^{19}F NMR Spectral Parameters

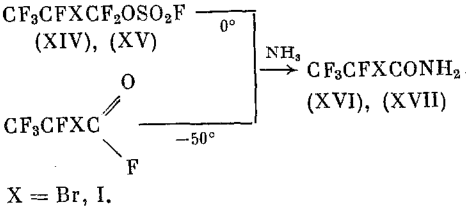
Compound	δ, ppm	J,Hz
$\mathrm{C\overset{1}{F_3}C\overset{2}{F}\overset{3}{H}CON\overset{4}{H}N(\overset{5}{CH_3})_2}$ (Ia)	δ_1 −1,45d.d., $\delta_2$124,14d.q., δ_3 4,21 d.q., δ_4 8,80br.s. δ_5 2,61s	J_{12}=11,0 J_{13}=7,4 J_{23}=44,5
$\mathrm{\overset{1}{H}C\overset{2}{F_2}C\overset{3}{F_2}CON\overset{4}{H}N\overset{4}{H}\overset{5}{C_6H_5}}$ (IIb)	δ_1 6,05t.t, δ_2 61,79d.t, δ_3 48,41 d.t, δ_4 10,31 br.s, δ_5 6,5–7,4m	J_{12}=54,2 J_{13}=J_{23}=7,3
$\mathrm{C\overset{1}{F_3}C\overset{2}{F}ClCON\overset{3}{H}N(\overset{4}{CH_3})_2}$ (IIIa)	δ_1 2,28d., δ_2 58,35 q, δ_3 8,80 br.s., δ_4 2,77 s	J_{12}=6,2
$\mathrm{C\overset{1}{F_3}C\overset{2}{F}ClCON\overset{3}{H}N\overset{3}{H}\overset{4}{C_6H_5}}$ (IIIb)	δ_1 1,95d., δ_2 57,50 q, δ_3 10,26 br.s, δ_4 6,7–7,1 m	J_{12}=6,8
$\mathrm{ClC\overset{1}{F_2}C\overset{2}{F_2}CON\overset{3}{H}N(\overset{4}{CH_3})_2}$ (IVa)	δ_1 −8,95 t, δ_2 39,47 t, δ_3 9,11 br.s, δ_4 2,70 s	J_{12}=4,5
$\mathrm{ClC\overset{1}{F_2}C\overset{2}{F_2}CON\overset{3}{H}N\overset{3}{H}\overset{4}{C_6H_5}}$ (IVb)	δ_1 −7,51 t, δ_2 40,78 t, δ_3 10,43 br.s, δ_4 6,7–7,4m	J_{12}=4,7
$\mathrm{(C\overset{1}{F_3})_2C\overset{2}{H}COO\overset{3}{CH_2}\overset{4}{CH_3}}$ (VIII)	δ_1−12,70d, δ_2 4,05 sep, δ_3 4,25 q, δ_4 1.30 t	J_{12}=J_{34}=6,8
$\mathrm{(C\overset{1}{F_3})_2C\overset{2}{H}CON\overset{3}{H}N(\overset{4}{CH_3})_2}$ * (XI)	δ_1 −11,99 q, δ_2 5,0sept, δ_3 8,70 br.s, δ_4 2,4 s	J_{12}=6,7
$\mathrm{(C\overset{1}{F_3})_2CClCON\overset{2}{H}N(\overset{3}{CH_3})_2}$ (XIII)	δ_1 −6,95 s, δ_2 9,20br.s, δ_3 2,84 s	
$\mathrm{C\overset{1}{F_3}C\overset{2}{F}BrCO\overset{3}{NH_2}}$ (XVI)	δ_1 −0,97 d, δ_2 55,50q, δ_3 7,95 br.s	J_{12}=8,7
$\mathrm{C\overset{1}{F_3}C\overset{2}{F}ICO\overset{3}{NH_2}}$ (XVII)	δ_1 −2,03 d, δ_2 61,45 q, δ_3 7,70 br.s	J_{12}=11,9

*Solution in $\mathrm{CF_3COOH}$.

Hydrazide (XI) was also obtained by convergent synthesis through the addition of DH to bis(trifluoromethyl)ketene.

$$\mathrm{(CF_3)_2C{=}C{=}O + H_2NNMe_2 \xrightarrow[\text{toluene}(-10^\circ)]{} (XI)}$$

The bromine and iodine atoms in 2-bromo- and 2-iodohexafluoropropyl fluorosulfate (XV) are not as mobile as in (VI), (VII), and (IX). Treatment of ethereal solutions of (XIV) and (XV) with anhydrous $\mathrm{NH_3}$ gives 2-bromo- (XVI) and 2-iodopropionamides (XVII) in yields above 80% which were also obtained by the reactions of the corresponding acid fluorides with ammonia.



X = Br, I.

In addition, we found that aqueous $\mathrm{NH_3}$ may be used for the synthesis of amides of polyfluorocarboxylic acids from PFS

$$\mathrm{(I), (II), (XIV), (XV) + NH_3(aq.) \rightarrow \underset{(XVI)-(XIX)}{R_FCONH_2}}$$

This reaction is general and applicable for the synthesis of diamides of higher perfluoroalkanedicarboxylic acids.

$$\mathrm{FSO_2O(CF_2)_{\mathit{n}}OSO_2F + NH_3(aq.) \rightarrow \underset{(XX)-(XXII)}{(CF_2)_{\mathit{n}-2}(CONH_2)_2}}$$

n = 6 (XX), 8 (XXI), 10 (XXII).

TABLE 2. Physical Constants of the Compounds Obtained

Compound	Yield, %	Mp, °C	Chemical formula	Found/Calculated, %			
				C	H	F	N
(Ia)	68	81–82	$C_5H_8F_4N_2O$	32,12 31,91	4,00 4,26	40,74 40,42	14,58 14,89
(IIb)	65	84–85	$C_9H_8F_4N_2O$	45,49 45,76	3,30 3,39	32,60 32,20	11,59 11,86
(IIIa)	78	91–92	$C_5H_7ClF_4N_2O$	26,51 26,97	2,90 3,15	34,17 34,16	12,33 12,58
(IIIb)	74	92–93	$C_9H_7ClF_4N_2O$	39,71 39,93	2,45 2,59	28,19 28,08	10,58 10,35
(IVa)	78	65–66	$C_5H_7ClF_4N_2O$	27,39 26,97	3,09 3,15	34,53 34,16	12,44 12,58
(IVb)	75	105–106	$C_9H_7ClF_4N_2O$	40,08 39,93	2,49 2,59	28,30 28,08	10,19 10,35
(Va)	83	55–56	$C_{10}H_7ClF_{14}N_2O$	25,10 25,40	1,42 1,48	56,48 56,29	5,96 5,93
(X)	72	154–155 *	$C_4H_3F_6NO$	24,71 24,62	1,80 1,54	58,73 58,46	6,73 7,18
(XI)	69	159–160	$C_6H_8F_6N_2O$	30,15 30,25	3,35 3,36	47,53 47,90	11,60 11,76
(XII)	79	81–82 *	$C_4H_2ClF_6NO$	21,12 20,91	1,08 0,87	49,89 49,67	5,95 6,10
(XIII)	79	105–106	$C_6H_7ClF_6N_2O$	26,10 26,42	2,41 2,57	41,55 41,83	10,12 10,30
(XVI)	83	83–84	$C_3H_2F_4BrNO$	16,22 16,08	1,05 0,89	34,08 33,94	6,23 6,25
(XVII)	78	88–78	$C_3H_2F_4INO$	13,33 13,29	1,01 0,74	28,43 28,05	5,43 5,17
(XVIII)	83	58–59 †	$C_3H_3F_4NO$	24,88 24,83	2,15 2,07	52,63 52,41	9,79 9,66
(XIX)	85	58–59 **	$C_3H_3F_4NO$	24,90 24,83	1,55 2,07	52,23 52,41	9,60 9,66

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*See the work of Aktaev [7].

†See the work of Aktaev [8].

**See the work of Atherton [9].

EXPERIMENTAL

The ^{19}F and ^{1}H NMR spectra were taken on a Hitachi R-20 spectrometer at 60 and 56.45 MHz in acetone relative to CF_3CO_2H as the external standard and HMDS (Table 1). The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph on a 3 m × 3 mm column packed with 30% DNF on Chromatone AW-DMCS (0.250-0.315) and a 3 m × 3 mm column packed with 5% QF-1 on Chezasorb AW-NMDS (0.200-0.250) with 18.5 ml/min helium gas flow rate. The yields, properties, and elemental analysis data for these products are given in Table 2.

Polyfluorocarboxylic acid hydrazides (typical experiment). A solution of 40 mmole PFS in 15 ml ether was added dropwise with stirring to a solution of 150 mmole DH (or phenylhydrazine) in 70 ml abs. ether at 0°C and stirred for 3 h at 20°C. The reaction mass was poured into 150 ml water. The organic layer was separated and the aqueous fraction was extracted with two 20-ml portions of ether. The combined extract was washed with water and dried over $MgSO_4$. The solvent was removed in vacuum at a water pump and the solid residue was sublimated at 1 mm.

Reaction of β-iodooctafluoroisobutyl fluorosulfate (VII) with NH_3. A sample of 4.5 liter anhydrous NH_3 was bubbled with stirring through a solution of 13.6 g (32 mmole) β-iodooctafluoroisobutyl fluorosulfate (VII) in 80 ml abs. ether. The reaction mass was poured into water and the organic layer was separated. The aqueous fraction was extracted with two 20-ml portions of ether. The combined extract was washed with water and dried over $MgSO_4$. Fractionation gave 2.1 g ethyl iodide, bp 70-72°C (identical to an authentic sample as shown by gas-liquid chromatography) and 5.5 g (VIII), bp 102-104°C, d_4^{20} 1.356, n_D^{20} 1.3142 [5].

Ethyl bromide and (VIII) were obtained under analogous conditions from β-bromooctafluoroisobutyl fluorosulfate (VI).

α-Hydrohexafluoroisobutyro-N,N-dimethylhydrazide (IX). A solution of 4 g (66.7 mmole) DH in 10 ml toluene was added dropwise with stirring to a solution of 12 g (67.4 mmole) bis(trifluoromethyl)ketene in 50 ml abs. toluene over 30 min at −10°C and then the solution was gradually warmed to 20°C. The crystals formed were filtered off and recrystallized from toluene to give 6.3 g (39.4%) (IX), mp 160°C. A mixed probe of hydrazide (IX) and a sample obtained by another method was undepressed.

Polyfluorocarboxylic acid amides (typical experiment). a) A sample of 4.5 liters (190 mmoles) ahydrous NH_3 was bubbled with stirring through a solution of 32 mmole PFS in 80 ml abs. ether for 5 h at 0°C. The mixture was poured into 150 ml water. The organic layer was separated and the water layer was extracted with two 20-ml portions of ether. The combined extract was washed with water and dried over $MgSO_4$. The solvent was removed at a water pump and the residue was recrystallized from hexane.

b) A sample of 50 mmole PFS was added dropwise with stirring to a mixture of 20 ml 25% aqueous NH_3 and 30 ml ether at 15°C over 0.5 h. Stirring was continued for 0.5 h at 35°C. The organic layer was separated and the mixture was worked up as in procedure a).

c) A sample of 15 mmole 2-halotetrafluoropropionyl fluoride was added dropwise to a solution of 50 mmole anhydrous NH_3 in 30 ml abs. ether at −50°C and then gradually warmed to 20°C. Then the mixture was worked up as in procedure a). The yield of propionamide (XVI) was 68% and the yield of propionamide (XVII) was 60%. Mixed probes of (XVI) and (XVII) with samples obtained by methods a and b gave undepressed melting points.

Perfluorodicarboxylic acid amides (typical experiment). A sample of 60 mmole α,ω-bis(fluorosulfonyloxy)perfluoroalkane was added to a mixture of 120 ml 25% aqueous NH_3 and 350 ml ether at 15°C and stirred for 5 h at 35°C. Ether was removed in vacuum at a water pump. The solid residue was filtered off, washed with two 150-ml portions of water and two 75-ml portions of freon-113, and recrystallized from DMF—water. The yields of (XX)-(XXII) were 80-85%, (XX), mp 236-238°C, (XXI), 237-239°C, (XXII), mp 238-241°C [6].

CONCLUSIONS

1. Polyfluoroalkyl fluorosulfates react with hydrazines and ammonia to form hydrazines and amides of the corresponding polyfluorocarboxylic acids.

2. Treatment of ethereal solutions of β-iodo- and β-bromooctafluoroisobutyl fluorosulfates by ammonia leads to the halogenation of the ester and formation of the ethyl ester of α-hydrohexafluoroisobutyric acid, and correspondingly, ethyl iodide or ethyl bromide.

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